Surface Scattering in Quantum Mechanics

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Matter exhibits wave-like properties at the microscopic scale, leading to scattering phenomena similar to those observed with light. This paper introduces a modeling methodology for predicting the scattering of quantum objects through surfaces using the Eikonal approximation in conjunction with binary potentials, and apply this methodology to electron scattering through graphene.

INTRODUCTION

Matter exhibits wave-like properties at the microscopic scale, resulting in scattering phenomena similar to those observed with light. This phenomenon has been experimentally demonstrated numerous times, notably in 1927 with the first diffraction of an electron beam through a thin film of platinum.

We will begin by introducing a method for predicting the intensity of scattering peaks, relying on the WKB and the Eikonal approximations. Furthermore, to be able to apply this method we will need the interaction potential between the surface and the incoming object, for this we will use the binary potential approximation. As an example, this methodology will be applied to the case of electron scattering through graphene.

I. PREDICTING THE INTENSITY OF SCATTERING PEAKS

A. Hamiltonian in Scattering Theory

In quantum mechanics, it is usual to begin by writing the Hamiltonian of the considered system. In the case of scattering, under the approximation that the scatterer is fixed, it is expressed as follows:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{W}(x, y, z), \tag{1}$$

where m is the incident object mass and $\hat{W}(x, y, z)$ is the interaction potential between the two objects under consideration.

B. Normal Incidence Surface Scattering: A Far-Field Solution

In this section, we will solve Schrödinger equation corresponding to Hamiltonian (1) for the case of an elastic collision with a periodic surface, such as graphene.

Firstly, noting that $W(x, y, z)$ is periodic in the (x, y) plane, we can assume that the wave function in the far-field will take the form of a Bloch wave with a phase denoting the lattice periodicity. Let's therefore try a solution of the form:

$$\psi(x, y, z) = \underbrace{\exp(ik_z z)}_{\psi_i} + \underbrace{\exp(i\mathbf{Q}\cdot\boldsymbol{\rho})\,\chi(z)}_{\psi_s}, \tag{2}$$

where $\mathbf{Q}$ and $\boldsymbol{\rho}$ are the reciprocal lattice vector and the real lattice vector parallel to the surface, respectively. Substituting this Ansatz into (1) yields:

$$\left[\partial_z^2 + k_{x,y}^2(z)\right]\chi(z) = 0, \tag{3}$$

where:

$$k_{x,y}^2(z) = k_z^2 - \|\mathbf{Q}\|^2 - \frac{2m}{\hbar^2}W(x, y, z). \tag{4}$$

Here, $k_{x,y}^2(z)$ can be interpreted as a screened wave vector. To proceed with our calculations, we will assume that $W(x, y, z)$ varies slowly with z (WKB approximation). Thus, a good Ansatz for a solution is:

$$\chi(z) = \exp\left(i\int_{-\infty}^{z} k_{x,y}(z')\mathrm{d}z'\right). \tag{5}$$

Furthermore, if we assume that the kinetic energy is significantly greater than the potential energy, implying that the trajectory is only weakly influenced by it, we have $\hbar^2 k_z^2/2m \gg W(x, y, z) \gg \hbar^2 |\mathbf{Q}|^2/2m$ and $k_z \approx k_z'$ (Eikonal approximation). This leads to:

$$\chi(z) \approx \exp\left(i\left[k_z z - \frac{m}{\hbar^2 k_z}\int_{-\infty}^{z} W(x, y, z')\mathrm{d}z'\right]\right). \tag{6}$$

Moreover, it is known that in the far-field the scattered wave function must be of the form [1]:

$$\psi_s(x, y, z) = \sum_{n,m} C_{n,m}\exp\left(i(k_z' z + \mathbf{Q}\cdot\boldsymbol{\rho})\right). \tag{7}$$

Thus, by again applying the Eikonal approximation to (7) and by equating both far-field solutions. It is easy to see that the intensity $I_{n,m} = |C_{n,m}|^2$ is given by:

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$$I_{n,m} = \left| \frac{1}{A} \iint_{\Omega} \mathrm{d}x\, \mathrm{d}y \overleftrightarrow{x} \overleftrightarrow{y} \exp\left(-\frac{i}{\hbar v_z} \int_{\mathbb{R}} W(x,y,z')\, \mathrm{d}z' \right) \right|^2 \tag{8}$$

where A is the surface of the unit cell Ω, $v_z = \hbar k_z / m$ and $\overleftrightarrow{j} = \exp(-i\mathbf{Q}\cdot\mathbf{j})$ with $\mathbf{j} \in \{\mathbf{x}, \mathbf{y}\}$. This expression for the intensity is reminiscent of the Fraunhofer equation for the far-field intensity of light diffraction.

II. INTERACTION POTENTIAL FOR ELECTRONIC SCATTERING

As we can see in (8), we need the interaction potential to compute the intensity. However, the interaction between the surface and an incoming object is too complex to be computed analytically, so one might approximate this interaction. In this section, we will examine the binary potential approximation, which suggests that the total potential can be approximated by the superposition of the potentials between each surface atom and the incident electron. First, let's start by deriving the scattering factor in the first-order Born approximation, which will allows us to derive the binary interaction potential for electronic scattering.

A. Scattering factor

In this section, we will consider the scattering of electrons onto a single atom. Let's start with Schrödinger's equation for a two-particle system [2]:

$$\left(\hat{H}_0 + \hat{W}\right) |\psi\rangle = \hat{E}\, |\psi\rangle . \tag{9}$$

Here, $\hat{W}$ is the interaction potential, $\hat{H}_0$ is the free particle Hamiltonian. By reordering this equation, we obtain:

$$\left(\hat{E} - \hat{H}_0\right) |\psi\rangle = \hat{W}\, |\psi\rangle . \tag{10}$$

We hope that this operator is invertible such that:

$$|\psi\rangle = \frac{\hat{W}}{\hat{E} - \hat{H}_0}\, |\psi\rangle . \tag{11}$$

However, here we might encounter poles, thus we will add a regulator to be able to perform this integral.

$$\left|\psi^{\pm}\right\rangle = \frac{\hat{W}}{\hat{E} - \hat{H}_0 \pm i\varepsilon}\, \left|\psi^{\pm}\right\rangle . \tag{12}$$

Here, the $\pm$ sign denotes causality. A positive sign represents the causal Green function, where waves emanate from the source and propagate outward to infinity, while a negative sign represents the anti-causal Green function, where waves originate from infinity and move inward toward the source. We will concentrate on the + case, as our interest is in scattered states.

$$\hat{G}^{+} = \frac{1}{\hat{E} - \hat{H}_0 + i\varepsilon}, \tag{13}$$

is known as the free particle Green function. Since our incoming particle is a plane wave, when $\hat{W} \to 0$, we should smoothly fall back to a plane wave, thus, (11) becomes:

$$\left|\psi^{+}\right\rangle = |\phi_{\mathbf{k}}\rangle + \hat{G}^{+}\hat{W}\, \left|\psi^{+}\right\rangle . \tag{14}$$

Where $|\phi_{\mathbf{k}'}\rangle$ is the free particle Schrödinger equation solution. Premultiplying by $\langle\mathbf{r}|$:

$$\psi^{+}(\mathbf{r}) = \phi_{\mathbf{k}}(\mathbf{r}) + \langle\mathbf{r}|\, \hat{G}^{+}\hat{W}\, \left|\psi^{+}\right\rangle , \tag{15}$$

and by using the resolution of the identity:

$$\psi^{+}(\mathbf{r}) = \phi_{\mathbf{k}}(\mathbf{r}) + \int \mathrm{d}\mathbf{r}'\, \langle\mathbf{r}|\, \hat{G}^{+}\hat{W}\, |\mathbf{r}'\rangle \left\langle\mathbf{r}'\middle|\psi^{+}\right\rangle . \tag{16}$$

Which can be simplified as:

$$\psi^{+}(\mathbf{r}) = \phi_{\mathbf{k}}(\mathbf{r}) + \int \mathrm{d}\mathbf{r}'\, \langle\mathbf{r}|\, \hat{G}^{+}\, |\mathbf{r}'\rangle\, W(\mathbf{r}')\psi^{+}(\mathbf{r}'). \tag{17}$$

We also know that $\langle\mathbf{r}|\, \hat{G}^{+}\, |\mathbf{r}'\rangle$ is equal to (Refer to appendix (A)):

$$\langle\mathbf{r}|\, \hat{G}^{+}\, |\mathbf{r}'\rangle = -\frac{2m}{\hbar^2} \frac{\exp\left(+ik\|\mathbf{r} - \mathbf{r}'\|\right)}{4\pi\|\mathbf{r} - \mathbf{r}'\|}. \tag{18}$$

Which, when, $\|\mathbf{r}'\| \ll \|\mathbf{r}\|$ is approximated as:

$$\langle\mathbf{r}|\, \hat{G}^{+}\, |\mathbf{r}'\rangle \approx -\frac{2m}{\hbar^2} \frac{\exp\left(+ikr - i\mathbf{k}'\cdot\mathbf{r}'\right)}{4\pi r}. \tag{19}$$

This approximation is justified if we consider the detector to be far away. Plugging it back into (17):

$$\psi^{+}(\mathbf{r}) = \phi_{\mathbf{k}}(\mathbf{r}) - \int \mathrm{d}\mathbf{r}' \frac{2m}{\hbar^2} \frac{\exp\left(+ikr - i\mathbf{k}'\cdot\mathbf{r}'\right)}{4\pi r} W(\mathbf{r}')\psi^{+}(\mathbf{r}'). \tag{20}$$

Which can be simplified as:

$$\psi^+(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}}\Big(\exp(i\mathbf{k}\cdot\mathbf{r}) - \frac{2m}{\hbar^2}\frac{(2\pi)^3}{4\pi}\frac{\exp(+ikr)}{r}\int \mathrm{d}\mathbf{r}'\frac{\exp(-i\mathbf{k}'\cdot\mathbf{r}')}{(2\pi)^{3/2}}W(\mathbf{r}')\psi^+(\mathbf{r}')\Big). \tag{21}$$

We will define the scattering factor $f(\mathbf{k},\mathbf{k}')$ as:

$$f(\mathbf{k},\mathbf{k}') = -\frac{2m}{\hbar^2}\frac{(2\pi)^3}{4\pi}\int \mathrm{d}\mathbf{r}'\frac{\exp(-i\mathbf{k}'\cdot\mathbf{r}')}{(2\pi)^{3/2}}W(\mathbf{r}')\psi^+(\mathbf{r}') = -\frac{2m}{\hbar^2}\frac{(2\pi)^3}{4\pi}\langle\phi_{\mathbf{k}'}|\hat{W}|\psi^+\rangle. \tag{22}$$

Finally, by premultiplying equation (14) by $\hat{W}$, we obtain:

$$\hat{W}|\psi^+\rangle = \hat{W}|\phi_{\mathbf{k}}\rangle + \hat{W}\hat{G}^+\hat{W}|\psi^+\rangle = \underbrace{\underbrace{\hat{W}|\phi_{\mathbf{k}}\rangle}_{\text{1st order}} + \hat{W}\hat{G}^+\hat{W}|\phi_{\mathbf{k}}\rangle}_{\text{2nd order}} + \dots \tag{23}$$

We see that this is a perturbative expansion. In our case, we will consider the first-order Born approximation, which involves taking only the first-order term. This approximation is valid for high-energy scattering, similar to the Eikonal approximation. However, it is particularly useful because it directly yields the Fourier transform of the potential:

$$f(\mathbf{k},\mathbf{k}') = -\frac{m}{2\pi\hbar^2}\int \mathrm{d}\mathbf{r}'\exp(i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}')\,W(\mathbf{r}'), \tag{24}$$

which can be rewritten as:

$$f(\mathbf{Q}) = -\frac{1}{2\pi a_0 e^2}\int \mathrm{d}\mathbf{r}'\exp(i\mathbf{Q}\cdot\mathbf{r}')\,W(\mathbf{r}'), \tag{25}$$

where $\mathbf{Q}$ is the momentum exchanged during scattering.

B. Interaction potential

We see that if we were able to find an expression for $f(\mathbf{Q})$, we could extract the interaction potential via inverse Fourier transform. Fortunately, parametrization of $f(\mathbf{Q})$ for electron scattering on an atom can be found in the literature [3]:

$$f(\mathbf{Q}) = \sum_{i=1}^{3}\frac{a_i}{\|\mathbf{Q}/2\pi\|^2 + b_i} + \sum_{i=1}^{3} c_i\exp\left(-d_i\|\mathbf{Q}/2\pi\|^2\right), \tag{26}$$

where the coefficients a_i, b_i, c_i, d_i can be found in [3]. Finally, by performing the inverse Fourier transform, we obtain an expression for the interaction potential between an electron and an atom:

$$W(r) = -2\pi^2 a_0 e^2\sum_{i=1}^{3}\frac{a_i}{r}e^{-2\pi r\sqrt{b_i}} - 2\pi^{5/2}a_0e^2\sum_{i=1}^{3}c_i d_i^{-3/2}e^{-\pi^2r^2/d_i}, \tag{27}$$

with $r = \sqrt{x^2+y^2+z^2}$.

III. APPLICATION: SCATTERING OF ELECTRONS THROUGH GRAPHENE

In this section, we apply earlier derivations to numerically predict the scattering pattern of electrons through graphene. Graphene is a two-dimensional surface composed of carbon atoms. We define our unit cell as illustrated below:

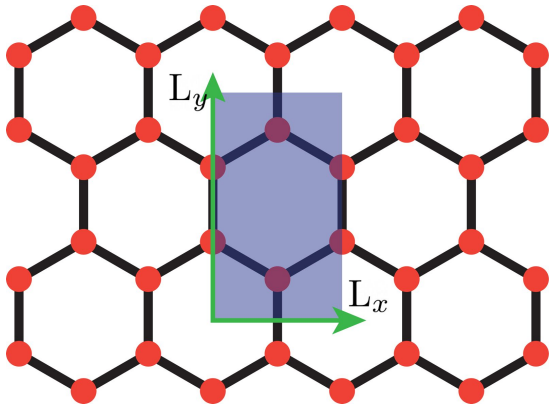

FIG. 1. Unit cell for the graphene layer.

The aforementioned parametrization coefficients for a carbon atom are the following:

i	a_i (Å^{-1})	b_i (Å^{-2})	c_i (Å)	d_i (Å^2)
1	0.212080767	0.208605417	0.199811865	0.208610186
2	0.168254385	5.57870773	0.14204836	1.33311887
3	0.363830672	3.80800263	0.000835012	0.040398262

TABLE I. Parametrization coefficients for a carbon atom.

Plotting the electric atomic potential, defined as $V(r) = -\frac{1}{e}W(r)$, yields:

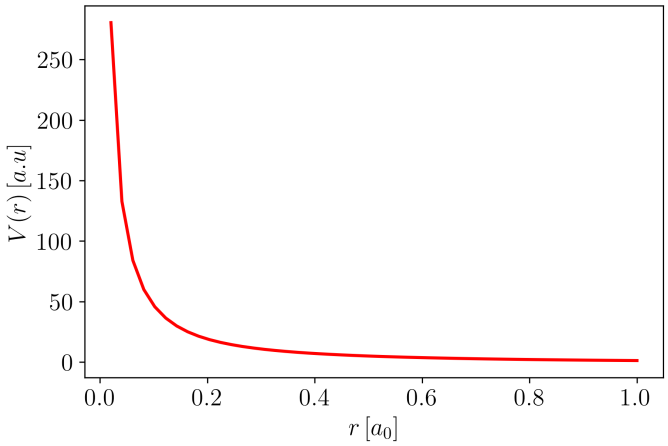

FIG. 2. Electric potential $V(r)$ of a carbon atom.

From this potential, it becomes possible to construct the potential of the unit cell. By numerically integrating this potential along z, we obtain:

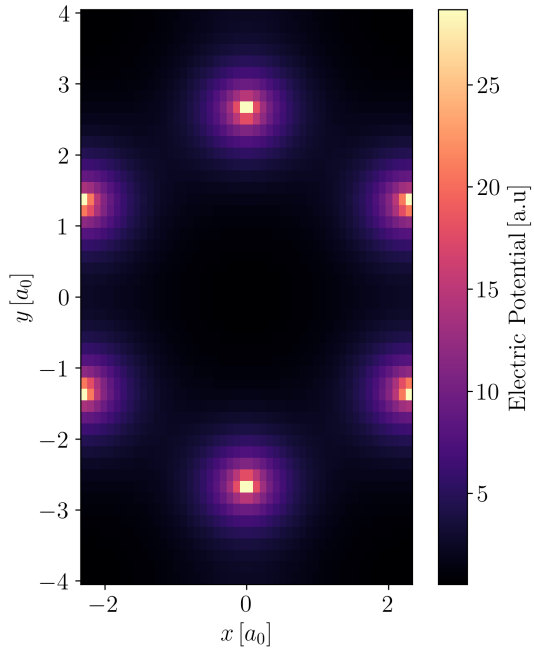

FIG. 3. Electric potential $V(r)$ of a graphene layer.

Finally, we now have all the necessary elements to compute the intensity of the scattering peaks using equation (8). By convolving each peak with a Gaussian, we obtain:

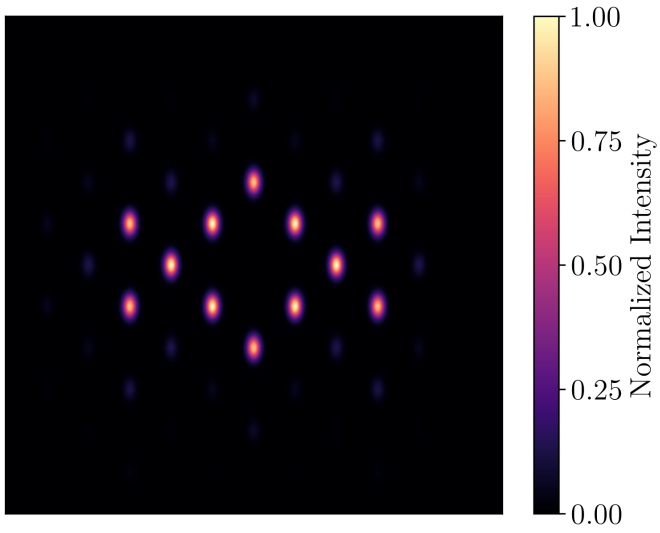

FIG. 4. Normalized scattering peaks' intensity of a 10 keV electron through graphene.

However, our method does not provide information about the spacing between peaks, only their intensity. Thus, the spacing between them is arbitrary.

CONCLUSION

To summarize, by employing multiple approximations, one can obtain the intensity of scattering peaks in the far-field at the cost of an interaction potential. In the case of electron scattering, a semi-analytical method exists to approximate this potential, where the coefficients are determined numerically. Using these methods, we were able to predict the scattering of an electron through graphene.

However, when it comes to predicting atom-surface scattering, the situation isn't analytical anymore. Consequently, only a few approaches exist to determine the atom-surface interaction potential, including:

1. Empirical binary potentials (e.g., Lennard-Jones, Morse)
2. Binary potentials derived from Density Functional Theory (DFT)
3. Full DFT potentials

However, the last approach is often too computationally intensive to be fully achieved.

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Appendix A: Free particle Green function in position representation

In this section we are going to prove relation (18) Firstly let's remind ourselves of the Green function operator:

$$\hat{G}^{+} = \frac{1}{\hat{E} - \hat{H}_0 + i\varepsilon}. \tag{A1}$$

We desire to evaluate the matrix element $\langle \mathbf{r}| \hat{G}^{+} |\mathbf{r}'\rangle$, let's start by inserting a resolution of the identity [2]:

$$\begin{aligned}
\langle \mathbf{r}| \hat{G}^{+} |\mathbf{r}'\rangle &= \langle \mathbf{r}| \hat{G}^{+} \int \mathrm{d}\mathbf{k}' \, |\phi_{\mathbf{k}'}\rangle \langle \phi_{\mathbf{k}'}| \mathbf{r}'\rangle \\
&= \frac{1}{(2\pi)^3} \langle \mathbf{r}| \hat{G}^{+} \int \mathrm{d}\mathbf{k}' \, |\phi_{\mathbf{k}'}\rangle \exp\left(-i\mathbf{k}' \cdot \mathbf{r}'\right) \\
&= \frac{1}{(2\pi)^3} \int \mathrm{d}\mathbf{k}' \, \langle \mathbf{r}| \frac{1}{\hat{E} - \hat{H}_0 + i\varepsilon} |\phi_{\mathbf{k}'}\rangle \exp\left(-i\mathbf{k}' \cdot \mathbf{r}'\right).
\end{aligned} \tag{A2}$$

Knowing that $\hat{H}_0^{-1} |\phi_{\mathbf{k}'}\rangle = 2m/\hbar^2 k'^2$ and by doing a change of variable of E as $\hbar^2 k^2/2m$:

$$\begin{aligned}
&= \frac{2m}{(2\pi)^3 \hbar^2} \int \mathrm{d}\mathbf{k}' \, \langle \mathbf{r}| \frac{1}{\mathbf{k}^2 - \mathbf{k}'^2 + i\varepsilon} |\phi_{\mathbf{k}'}\rangle \exp\left(-i\mathbf{k}' \cdot \mathbf{r}'\right) \\
&= \frac{2m}{(2\pi)^3 \hbar^2} \int \mathrm{d}\mathbf{k}' \frac{1}{k^2 - k'^2 + i\varepsilon} \exp\left(i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}')\right) \\
&= \frac{2m}{(2\pi)^2 \hbar^2} \int_{-\infty}^{+\infty} \mathrm{d}k' \frac{k'}{i\|\mathbf{r} - \mathbf{r}'\|} \frac{\exp\left(ik'\|\mathbf{r} - \mathbf{r}'\|\right)}{k^2 - k'^2 + i\varepsilon}.
\end{aligned} \tag{A3}$$

We can rewrite this integral as a contour integral. The contribution from the semicircular complex contour at infinity vanishes because the integrand decays sufficiently fast as $|k'| \to \infty$ (for complex-valued k'). Therefore, we can extend the integral from the real axis to the complex plane by considering a suitable contour that encircles the poles. Such contour is drawn below:

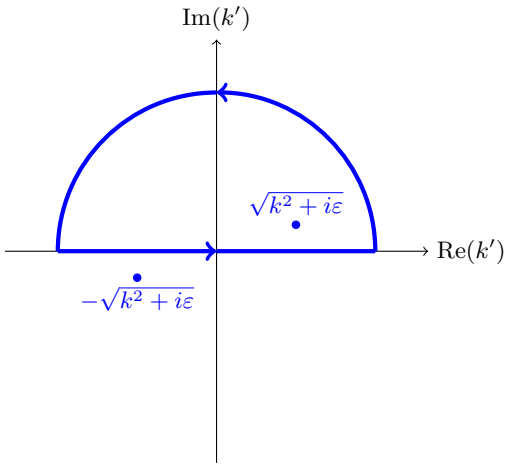

FIG. 5. Complex k' plane with integration contours and poles.

We will consider the blue semicircle as our contour:

$$\begin{aligned}
\langle \mathbf{r}| \hat{G}^{+} |\mathbf{r}'\rangle &= \frac{2m}{(2\pi)^2 \hbar^2} \int_{-\infty}^{+\infty} \mathrm{d}k' \frac{k'}{i\|\mathbf{r} - \mathbf{r}'\|} \frac{\exp\left(ik'\|\mathbf{r} - \mathbf{r}'\|\right)}{k^2 - k'^2 + i\varepsilon} \\
&= \frac{2m}{(2\pi)^2 \hbar^2} \frac{2\pi}{\|\mathbf{r} - \mathbf{r}'\|} \mathrm{Res}\{k' \frac{\exp\left(ik'\|\mathbf{r} - \mathbf{r}'\|\right)}{k^2 - k'^2 + i\varepsilon}, \sqrt{k^2 + i\varepsilon}\} \\
&= -\frac{m}{2\pi\hbar^2} \frac{\exp\left(ik\|\mathbf{r} - \mathbf{r}'\|\right)}{\|\mathbf{r} - \mathbf{r}'\|}.
\end{aligned} \tag{A4}$$

Which concludes the proof.

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[2] J. J. Sakurai and J. Napolitano, *Modern quantum mechanics*, 3rd ed. (Cambridge University Press, 2020) Chap. 6.

[3] E. J. Kirkland, Atomic potentials and scattering factors, in *Advanced Computing in Electron Microscopy* (Springer US, Boston, MA, 2010) pp. 243–260.